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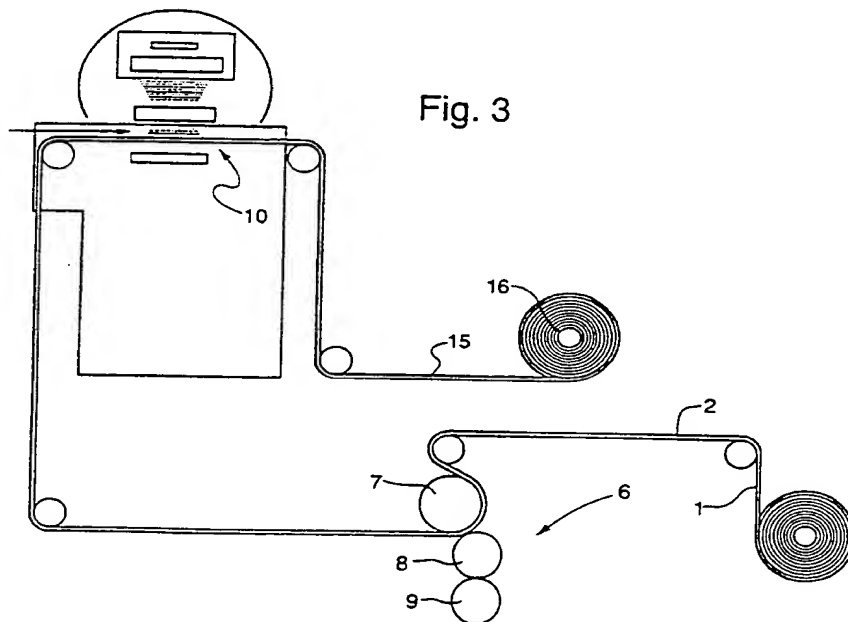
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## (54) Wearlayer/film composites for floor coverings

(57) A vinyl film is provided with an electron beam cured wearlayer. The preferred coated printed film is prepared by applying a polyester urethane acrylate composition to a printed sheet of rigid vinyl film (1) and exposing the coating to a low energy electron-beam, forming an abrasion-resistant topcoat with no substantial degradation of the printed rigid vinyl film.

The film is coated in a reverse roll coater using an applicator roll 8 and cured in electron beam unit (10). The wearlayer/film composite is laminated to a base, to provide floor tiles or floor covering sheets.



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Fig. 1

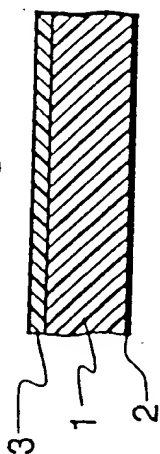


Fig. 2

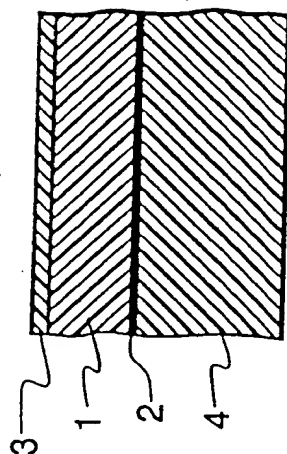


Fig. 3

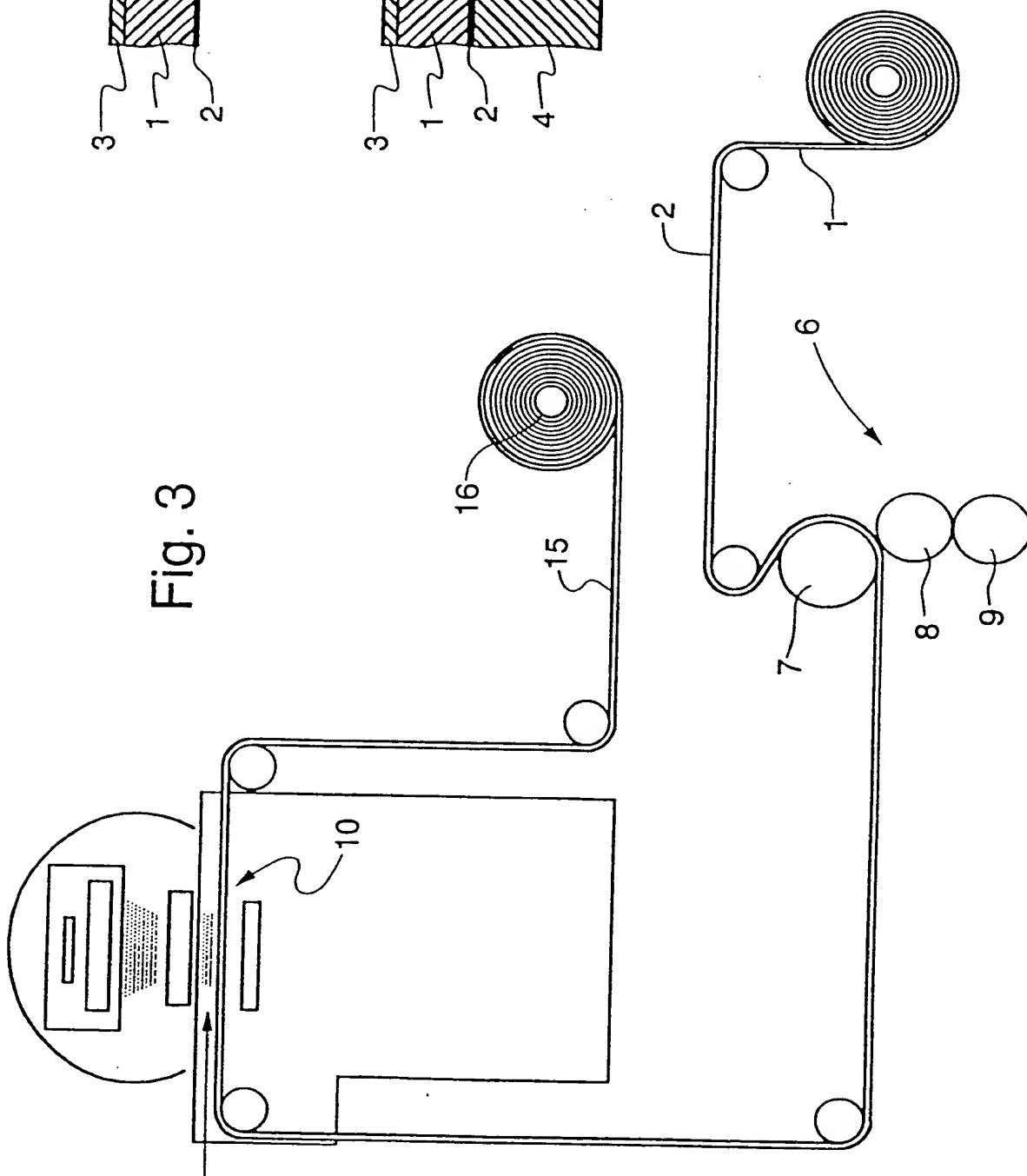
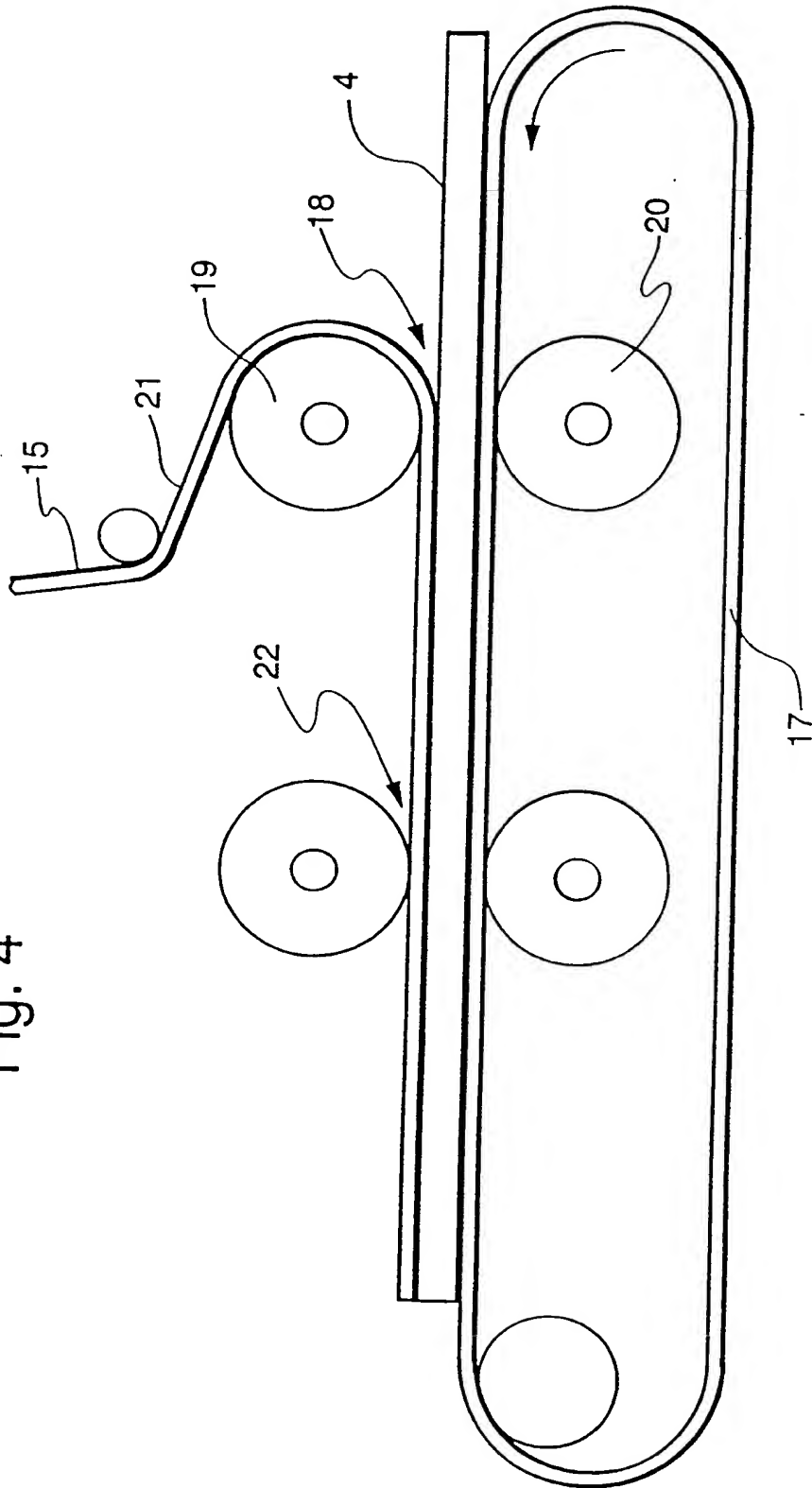


Fig. 4



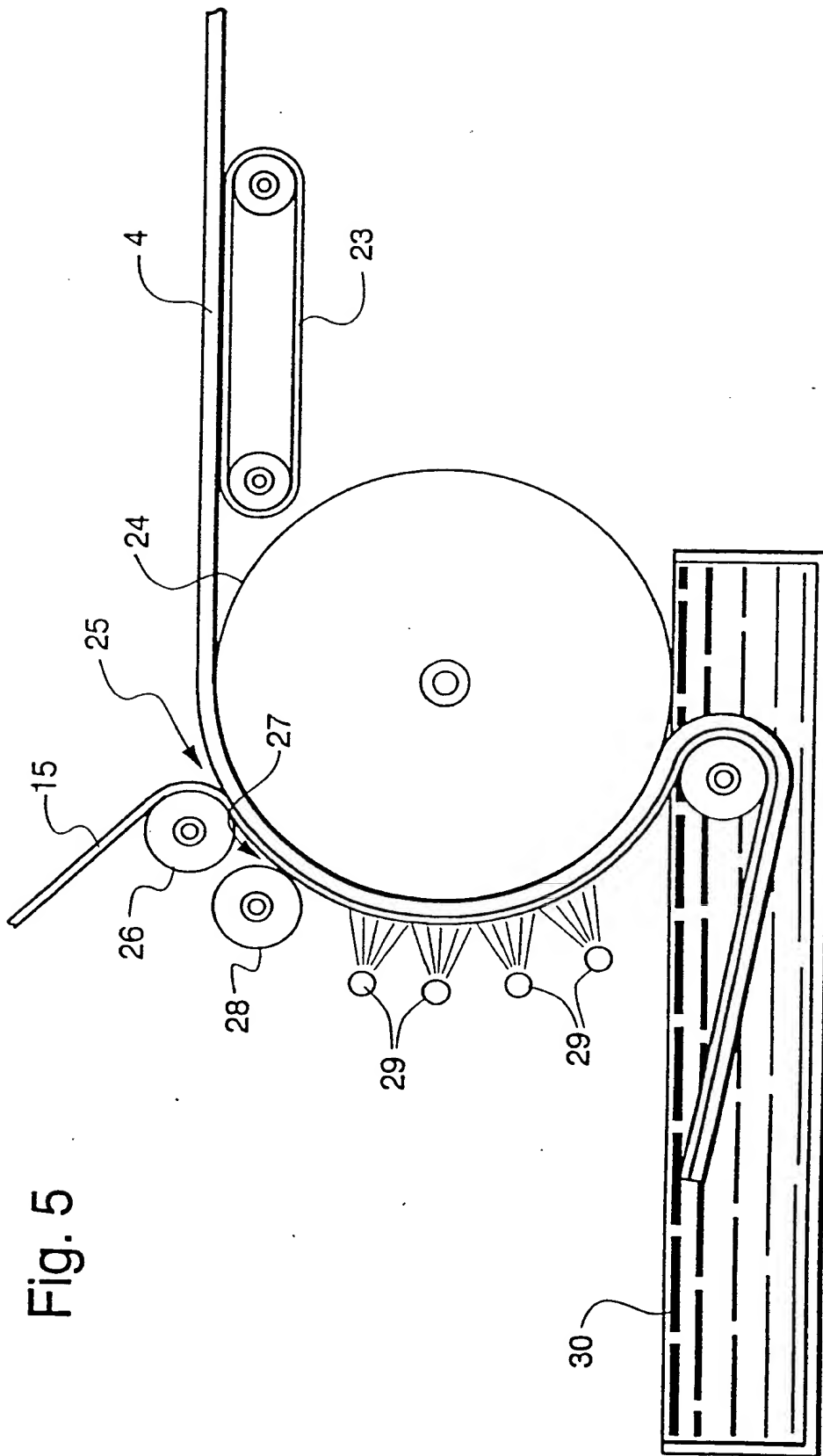


Fig. 5

SURFACE COVERING AND PROCESS FOR ITS MANUFACTURE

This invention relates to a surface covering, advantageously to a floor covering product, in which a wearlayer composition, preferably an acrylated urethane composition, is coated onto an underlying layer, especially a layer in film form, and more especially a polyvinyl chloride (PVC) or vinyl composition film, preferably a rigid vinyl film, to form a composite. In one embodiment, the composite is laminated to a surface covering substrate and embossed. If the product is a floor covering product it may be a floor tile or a floor covering sheet. The invention also relates to a process for the manufacture of the surface covering; in a preferred process, the composite is laminated to the substrate on a belt or drum line to form the final product.

It is common in the manufacture of a surface covering to include as a final or external layer of a multi-layer covering a, usually transparent, layer, which because its primary function is to protect the underlying layer, which is usually a decorative layer, is termed a wearlayer. The wearlayer is desirably cured, or crosslinked. It has been considered to use ultraviolet radiation to effect curing; this has, however, not proved satisfactory for the following reasons:

moiety, the film comprising a vinyl composition, the film having a thickness of no greater than about 0.5 mm, the wearlayer composition having been cured with electron beam radiation, and the film having a Delta b of no greater than 2 as measured before coating of the wearlayer composition and after curing of the wearlayer composition.

The invention further provides a process of making a surface covering comprising the steps of:

- a. providing a sheet of vinyl film material,
- b. coating the sheet with a wearlayer composition comprising a cross-linkable organic moiety, and
- c. curing the wearlayer composition with electron beam radiation, the electron beam radiation having an energy level of less than 135 KeV with a 7.0 cm average gap, and preferably at least 100 KeV with a 7.0 cm average gap.

At an average gap between the window and the substrate of 7.0 cm, a typical electron beam unit will lose approximately 10 KeV per 2.54 cm gap of accelerating energy in a typical nitrogen atmosphere. Hence the effect of an electron beam machine operating at 125 KeV with a gap of 7.0 cm will be similar to that of another similar machine operating at 105 to 110 KeV with a gap of 2.54 cm. Those skilled in the art will be able to determine, either by calculation or routine experiment, the appropriate conditions for the effect in a machine

an aesthetically acceptable composite and then the sheet is cut into floor tile.

"Rigid vinyl film" is a term of art which means a polyvinyl chloride film having fewer than 5 parts plasticizer per hundred parts by weight of resin (phr). Preferably, there is substantially no added plasticizer in the rigid vinyl film.

The accompanying drawings illustrate various embodiments of the invention.

Figure 1 is a cross-section of one form of wearlayer/film composite of the present invention.

Figure 2 is a cross-section of one form of laminated surface covering of the present invention.

Figure 3 is a schematic representation of a process for making a wearlayer/film composite of the present invention.

Figure 4 is a schematic representation of a process to laminate and emboss wearlayer/film composite of the present invention to a substrate.

Figure 5 is a schematic representation of a second process to laminate and emboss a wearlayer/film composite of the present invention to a substrate.

Referring to Figure 1, a wearlayer/film composite of the present invention has a polyvinyl chloride film base 1. In the preferred embodiment, the base is a rigid vinyl film which is printed on one side with an ink layer 2. The wearlayer 3 is a cross-linkable organic

The temperature of the rolls is kept well below the glass transition temperature of the film, e.g., 176°F (80°C), but warm enough to maintain the resin viscosity low enough to provide for improved flow characteristics, thereby eliminating coating defects commonly observed with high viscosity coatings.

The coated film enters the nitrogen inerted processing zone 10 of the electron beam unit where energetic electrons initiate radical polymerization of the ethylenic groups of the coating composition. After the wearlayer is cured, the wearlayer/film composite 15 is rolled onto a small diameter windup core 16.

The wearlayer resin composition used in this invention is chosen to exhibit performance properties sought in the surface covering. For floor covering products, the wearlayer properties include good stain resistance and gloss retention as well as sufficient toughness to resist gouging from foot wear traffic. For the purpose of this invention, the floor coverings must also display a certain degree of flexibility. A non-flexible floor covering that exhibits low elongation can result in the formation of across machine direction fractures once the composite film is wound onto the core.

Although not limited to polyurethane polyester, resin compositions that are useful as the wearlayer composition of this invention include the reaction product of a diisocyanate and/or isocyanurate structure,



ionizing radiation in the form of low energy accelerated electrons. This method, referred to as electron beam (EB) curing, requires that a nitrogen or other inert atmosphere be above the coating to be cured since the presence of oxygen in high concentrations will result in an undesirable tacky surface.

Since heat in the form of infra-red energy is essentially eliminated by using accelerated electrons, the substrate may be kept below its glass transition temperature and remain free of distortion while the wear layer composition is fully cured.

Typically, commercially available self-shielded electron beam units (Energy Science Inc., or RPC Industries) operate to produce an electron accelerating energy between 150,000 to 500,000 electron volts (150 KeV to 500 KeV). In curing applications where the preferred coating weight is 60 grams per meter square, more than 90 percent of the electrons penetrate into the substrate at an electron energy of 150 KeV. Such energy is sufficient to cause degradation of the rigid vinyl film and result in a yellow appearance that alters the decorative appeal.

Utilizing low electron beam accelerating energy of less than 135,000 electron volts, and preferably no greater than about 130,000 electron volts (assuming an average gap of substrate to window of 7.0 cm) has been found to limit electron penetration into the vinyl film and minimize yellowing of the vinyl film. This is

plate. For a wearlayer/PVC film composite, an effective method to clean the ink and substrate material from the composite is to wipe it, using a small brush, with a 2:1 volume ratio of isopropyl acetate:tetrahydrofuran, then with an isopropyl acetate solution, and finally with warm water.

If a Minolta CR300 colorimeter and a Minolta Calibration Plate No. 1933014 are used, typical values of +b for a product in accordance with the present invention are 2.90 for the cleaned composite on the calibration plate and 1.90 for the calibration plate alone. The product Delta b is accordingly 1.00.

A Delta b difference (either curing Delta b or product Delta b) greater than 1 can generally be detected by the naked eye. A Delta b difference greater than 2 is objectionable.

The 'dose' or amount of ionizing radiation is referred to as a 'rad', one rad being equal to 100 ergs of energy absorbed from ionizing radiation per gram of material. More commonly used terminology is a 'Megarad' (Mrad) or  $10^6$  rad. The dose required to cure the coating will be dependent on the chemistry of the coating and line speed. In the current application, a uniform dose of 2 to 4 Megarad is sufficient to cure the resin material.

The third step in the preferred process is lamination/embossing of the precoated decorative PVC film to a surface covering base. Two preferred methods for

the second nip, the surface of the rigid film/base is cooled by pouring water onto the film/base to reduce the product temperature to below the glass transition temperature of the rigid film 15. Stresses that developed during processing as a result of heat will be locked in to afford a flat floor covering structure.

Floor tile may be processed on a drum line. Referring to Figure 5, the vinyl base sheet 4, maintained at a temperature of 300°F (149°C) to 340°F (171°C), is transferred from a conveyor 23 to a drum 24 that is heated to 180°F (82°C) to give good adherence of the vinyl base sheet. The vinyl sheet 4 is fed through the first nip 25 formed by lamination roll 26 and the drum 24. The coated decorative PVC film 15 is fed into the first nip with the exposed side of the film being the side opposite the wearlayer.

In the first nip, the precoated film and base sheet are laminated. Then the coated rigid film/vinyl base mixture is fed through a second nip 27 formed by embossing roll 28 and the drum 24 to give the product an embossed texture. The temperature of the precoated film/vinyl mixture is kept above the glass transition temperature of the film and coating during the embossing process.

The laminated structure is then cooled by pouring water onto the surface with spray heads 29 while the laminated structure is in contact with the drum. The

nitrogen flow of about 28 liters per hour.

The reaction mixture was cooled and the total amount of water collected was 643 grams. The final product, Polyester 1, had an acid no. of 2.5 and a hydroxyl no. of 207. It therefore had a hydroxy equivalent weight of 274, and an estimated number average molecular weight of 880.

Polyester 1 was acrylated as follows. The materials listed below were introduced into a 2000 ml flask equipped with a mantle, stirrer, thermometer, gas inlet tube, dropping funnel, and Barrett Trap with a water cooled condenser on top.

Heptane	100 ml
Polyester 1	800 ml
Acrylic acid	277 g
Monomethyl ether of hydroquinone	0.1 g
p-Toluenesulfonic acid	5.38 g
Phosphorous acid	0.6 g
Hydroquinone	0.1 g
2,6-Di-tert-butyl-4-methylphenol	0.1 g

The trap was filled to the overflow with heptane. With dry air flow of about 5 liters per hour, the ingredients were heated to reflux at 210°F (98°C) to 221°F (105°C) while stirring vigorously and collecting water and displacing heptane in the trap. Heptane was added through the dropping funnel as required to maintain

the following charge weights:

1,6-Hexanediol	1058 g
Isophthalic acid	356 g
Glycerine	5 g
Adipic acid	582 g
Dibutyltin bislauryl mercaptide	0.4 g

The reaction mixture was cooled and water collected. The final product had an acid no. of 0.10 and a hydroxyl no. of 181. Therefore, it had a hydroxyl equivalent weight of 312.

#### WEARLAYER COATING COMPOSITION 1

A polyurethane floor covering wearlayer composition was prepared from the following charge in a 5 liter flask equipped with heating mantle, stirrer, and dry air purge at about 0.7 liters per hour:

Polyester 3	1111 g
Hexanediol diacrylate	341 g
2-Hydroxyethyl acrylate	409 g
2,6-Di-tert-butyl-4-methylphenol	0.72 g
Dibutyltin bislauryl mercaptide	6.3 g
4,4-dicyclohexylmethane diisocyanate	96 g

for ethoxylated triacrylates sold by Sartomer. The mixture was heated to 100°F (36°C) and 87 grams of an isocyanurate ring compound based on hexamethylene diisocyanate sold by Bayer under the trademark Desmodur N-3300, were added. The mixture was heated to 185°F (85°C) and maintained at this temperature for five hours. The mixture was cooled and to the flask were added:

Monomer mixture of ethoxylated triacrylates	15 g
Silicone surfactant	1 g

The monomer mixture was the same as identified above. An infrared spectrum confirmed that all of the NCO groups had reacted.

#### WEARLAYER COATING COMPOSITION 3

A polyurethane floor covering wearlayer composition was prepared from the following charge in a 3 liter flask equipped with heating mantle, stirrer, and dry air purge at about 0.7 liters per hour:

Polyester 2	180 g
Hydroxyalkyl acrylate	666 g
Isocyanurate ring compound	470 g

1.1 mm in thickness was provided on the conveyor such as shown in Figure 4 at a temperature of 300-320°F (149-160°C). The belt was heated to enable good adherence of the sheet to the belt. This belt line consisted of two sets of rolls used for lamination and embossing processes. The coated film was fed into the first nip with the coated side against the laminator roll. The partially distorted ultra violet (UV) cured coated film adhered to the laminator roll and did not release and laminate to the tile base. No acceptable tile product could be prepared by this method.

#### EXAMPLE 1

Wearlayer coating composition 1 containing no photoinitiator was applied at room temperature onto a 33 cm wide decorated rigid vinyl film, similar to the film of Comparative Example 1, by using a precision reverse three roll coater. The coating application yielded a 50 micron coating. This coated film was routed through an Energy Science Electro-Curtain machine operating at 125 KeV with a 7.0 cm average gap between the titanium electron beam window and the wearlayer/film composite at a line speed of 1.5 meters per minute. The dosage was 1.4 Mrad and the level of oxygen within the nitrogen inerted chamber where the coating was cured was kept below 50 parts per million. Color measurements were made on the cured film and the curing Delta b value computed based on

an Energy Science Electro-Curtain machine operating at 125 KeV with a 7.0 cm average gap between the titanium electron beam window and wearlayer surface at a line speed of 1.5 meters per minute. The dosage was 3.6 Mrad and the level of oxygen within the nitrogen inerted chamber where the coating was cured was kept below 50 parts per million.

Color measurements were made on cured white decorated film and the Delta b value computed based on change in yellowness during coating and curing (at low accelerating energy of 125 KeV) of the composite rigid vinyl film. The curing Delta b value was 0.60. The final roll of precoated white, decorative rigid vinyl film was processed on the same type of belt line as described in Example 1.

### EXAMPLE 3

Wearlayer Coating Composition 2 was applied onto a 33 cm wide decorative rigid film at a nominal thickness 1.0 to 1.15 microns. The coated film was routed through an Energy Science Electro-Curtain machine operating at 125 KeV with a 7.0 cm average gap between the titanium electron beam window and wearlayer surface at a line speed of 1.5 meters per minute. The dosage was 3.3 Mrad and the level of oxygen within the nitrogen inerted chamber where the coating was cured was kept below 50 parts per million.

Color measurements were made on the cured film and



adherence of the vinyl mixture to the drum was achieved.

At about the 11 o'clock position (as shown in Figure 5) on the drum, the vinyl mixture was fed through the first nip formed by the laminator roll 26 and the drum roll 24. The coated decorative rigid vinyl film 15 with the wearlayer coated side against the laminator roll 26 met the vinyl mixture sheet 4 at the nip and film and sheet were laminated.

Then at about the 10 o'clock position, a second embossing roll 28 formed a nip with the drum 24 and provided an embossed effect on the surface of the precoated decorative rigid vinyl film.

At about the 9 o'clock position, water was sprayed onto the coated rigid film/sheet to cool the surface of the film to approximately 150°F (66°C). The coated film/sheet laminate passed through water bath 30 where the temperature was further reduced below the glass transition temperature of the rigid vinyl film. The laminate was then cut into tiles.

#### EXAMPLE 5

An experimental abrasion resistant 100% solids inorganic/organic (colloidal silica/acrylate) coating supplied by SDC Inc. of Anaheim, California, was applied at room temperature onto a 33 cm wide decorative rigid vinyl film with an offset gravure coater equipped with a smoothing bar. This coated film was routed through an Energy Science Electro-Curtain machine operating at 120

of 3.3 Mrad. The cured coated film sections were analysed for color variation by utilizing a Minolta Colorimeter. Tristimulus color values are summarized as Delta b for each of the examples:

	KeV	Mrad	Delta b
Example 7	125	3.3	0.94
Example 8	130	3.3	1.81
Example 9	135	3.3	2.25

Electron beam curing at an electron beam accelerating energy of 125 KeV did not result in any significant yellowing of the coated white decorative film as indicated by the Delta b value of 0.94 in Example 7. Increasing the accelerating energy to 130 KeV resulted in slight yellowing of the decorative film as evident by a 100% increase in the Delta b value to 1.81 for Example 8. Electron beam curing the coated film at an accelerating voltage of 135 KeV in Example 9 resulted in objectionable yellowing of the decorative film in comparison to the 125 KeV processed sample, e.g., 0.94 versus 2.25 at 135 KeV.

to 3, wherein the wearlayer organic moiety prior to cross-linking is an ethylenic moiety, an epoxide moiety, of a mixture of such moieties.

5. The surface covering of claim 4, wherein the moiety is an acrylic moiety.

6. The surface covering of any one of claims 1 to 5, wherein the wearlayer composition comprises an acrylated urethane.

7. The surface covering of any one of claims 12 to 6, wherein the wearlayer has a thickness of 25 to 76 microns.

8. The surface covering of any one of claims 1 to 7, wherein the film has a thickness of less than about 0.25 mm.

9. The surface covering of claim 8 wherein the film has a thickness of 25 to 76 microns.

10. The surface covering of any one of claims 1 to 9, wherein the film is a rigid vinyl film.

11. The surface covering of any one of claims 1 to 10, wherein the film is capable of yellowing to an

17. The process of any one of claims 14 to 16, wherein the energy level of the electron beam radiation is no greater than 130 KeV with a 7.0 cm average gap.

18. The process of any one of claims 14 to 17, wherein the film has a curing Delta b of no greater than 2 when measured before and after curing of the wearlayer composition.

19. A process of making a surface covering, substantially as described with reference to and as illustrated by one of or more of the Figures in the accompanying drawings.

20. A process of making a surface covering, carried out substantially as described in any one of Examples 1 to 8 herein.

21. A surface covering whenever made by a process as claimed in any one of claims 14 to 20.

22. A surface covering substantially as described in any one of Examples 1 to 8 herein.

23. Any new feature disclosed herein or any new combination of hereindisclosed features.